

We might say that the Earth has the spirit of growth;
that its flesh is the soil.

Leonardo da Vinci (1452–1519)

AIR POLLUTION

The Oxidative Punch of Wildfires

Thick smoke routinely cloaks Southern California hills, highways, and neighborhoods during this region's autumn wild-fire season, with drought contributing to worse fires than usual in the past two years. Wildfire emissions generate larger aerosols than those produced by vehicles—up to 0.4 micrometers (μm) in diameter compared with less than 0.15 μm —according to a new study led by Constantinos Sioutas, a professor of civil and environmental engineering at the University of Southern California, Los Angeles. In findings published online 6 January 2009 ahead of print in *Environmental Science & Technology*, the larger particles emitted by fires activated a standard assay of oxidative stress even more potently than traffic pollutants. The performance of different types of particulate matter

in oxidative stress tests may provide clues as to how these pollutants cause damage such as proinflammatory or cytotoxic effects.

Sioutas and colleagues took advantage of wildfires burning in Southern California in October 2007 to investigate their impact on urban air quality relative to traffic pollutants, with a special emphasis on particulate matter small than 2.5 μm in diameter ($\text{PM}_{2.5}$). The researchers collected air samples on the University of Southern California campus, within 150 meters of a busy freeway near downtown Los Angeles. A series of wildfires had started on 20 October 2007, burning more than 500,000 acres of land and stretching from Santa Barbara County to the Mexican border. When air samples were collected on October 24, 25, and 27, fires were raging within 20 miles of the collection site. Measurements were taken from 4:30 P.M. until 10:30 A.M. the following day to capture pollution from evening and morning rush hour traffic as well as from the fires themselves. The fires in

Los Angeles County were under control by October 30; post-fire samples collected on November 1 and 14 represented mostly traffic emissions.

Compared with post-fire samples, samples collected on the three fire days in October contained a higher number of particles larger than 0.1 μm in diameter. Both carbon monoxide and nitrogen monoxide levels increased by threefold during fire days, while levels of other air pollutants—ozone, nitrogen dioxide, most polycyclic aromatic hydrocarbons, iron, copper, chromium, zinc, nickel, and vanadium—remained the same. In addition, during the fire period there was an approximate doubling in several indicators for biomass burning: levoglucosan, water-soluble organic carbon, and various minerals (magnesium, phosphorus, potassium, and manganese).

Various chemical components of $\text{PM}_{2.5}$ fuel oxidative stress and are toxic

to human cells. Working in collaboration with James Schauer of the University of Wisconsin–Madison and Flemming Cassee of the National Institute of Health and the Environment of the Netherlands, the Sioutas team measured cellular toxicity with two standard tests of oxidative stress, the dithiothreitol (DTT) assay and the macrophage reactive oxygen species (ROS) assay. Particles collected during October showed nearly 5 times more DTT activity than those collected in November. In contrast, the macrophage ROS assay, a known indirect measure for combustion pollutants from vehicles that is more responsive to transition metals, peaked in November.

“In this study we demonstrated that a substantial portion of the oxidative potential of air pollution during fires can be attributed to the wildfires,” says Sioutas. He attributes the difference to the increased water-soluble organic compounds that are abundant in wood smoke and show more activity in the DTT assay. According to Sioutas, the elevated levels of water-soluble organic carbon also mean wood smoke particles are more readily absorbed by the body than is PM from traffic sources.

The DTT and macrophage ROS assays “appear to respond to different components of $\text{PM}_{2.5}$,” notes Ted Russell, a professor of environmental engineering at the Georgia Institute of Technology in Atlanta. This observation suggests that environmental scientists need to further characterize the two redox assays. A detailed analysis of how these assays respond to specific $\text{PM}_{2.5}$ components obtained from different environmental samples at different times “will lay a foundation for understanding the characteristics of ambient $\text{PM}_{2.5}$ that have the greatest health impacts,” says Russell.

Sioutas says that the larger particles from wildfires can persist longer in the atmosphere and infiltrate buildings about twice as effectively as traffic pollutants. He recommends that people living near wildfires try to remain inside, shut their doors and windows, and run an air conditioner with a good filter to recirculate the indoor air. “If you don’t have an air conditioner, go to an indoor mall or other public place that recirculates indoor air,” he says. Other practical suggestions are included in the State of California guidelines for wildfire smoke at <http://www.arb.ca.gov/smp/progdev/pubeduc/wfgv8.pdf>. —Carol Potera

Wildfires burn near a neighborhood in Orange County, California, 24 October 2007.



CLIMATE CHANGE

Will Warmer Soil Be as Fertile?

Growing concern about global climate change has focused increasing research attention on the carbon-regulating role played by soil. Collectively, the Earth's soils contain more than twice the amount of carbon found in the atmosphere. Scientists at the University of Toronto Scarborough (UTS) now report that global warming may significantly alter soil composition at the molecular level and that such changes could have a major impact on atmospheric levels of carbon dioxide (CO₂).

Organic matter, the decaying remains of plants and animals, enables soil to support plant life, providing plants and soil microbes with the energy and raw materials they need for growth. Soil microbes facilitate the decomposition of organic matter from litterfall (the leaves, twigs, and other plant materials that fall to the ground), and CO₂ is a natural by-product of this process. Rising atmospheric temperatures and/or CO₂ levels are likely to increase photosynthesis and plant productivity, according to the results of several studies over the past two decades; consequently, litterfall is expected to increase. Until now, however, the effects of warming on soil's molecular composition have been poorly studied. It is therefore unclear to what extent the carbon-containing components of soil matter will accumulate or degrade and thus how much carbon will be sequestered by the soil and how much released into the atmosphere as CO₂.

In a report published online 23 November 2008 ahead of print in *Nature Geoscience*, environmental chemist Myrna Simpson and her UTS colleagues wrote that rising temperatures would be expected to speed up the decomposition of labile (easily degraded) soil organic compounds such as the carbohydrates from leaf litter, whereas more biochemically resistant carbon-containing structures—such as the lignin from woody tissues and lipids from leaf cuticles—would be expected to remain stable over decades, possibly even centuries. Nevertheless, says Simpson, global warming may change present-day decomposition patterns by altering the soil microbial communities and activities, thus changing the overall flow of carbon into and out of the soil and affecting soil fertility as well. She and her colleagues therefore attempted to discern how such a transition might unfold from the molecular perspective.

Their experiment took place in a moist mixed forest in southern Ontario close to the UTS campus. The site was separated into a control plot and a treatment plot, each measuring 4 meters by 4 meters. The soil temperature was unaltered in the control plot, while the test plot was heated through a series of steel pipes running through the ground. Temperature differences between the control and treatment plots were 3.5–4.5°C in the summer, spring, and autumn, and 5–6°C in the winter. The team carried out a detailed analysis of molecular changes in soil organic matter using a combination of gas chromatography/mass spectrometry, nuclear magnetic resonance, and total organic carbon analysis.

They found that the activity of some microorganisms increased in the warmer soil, resulting in a faster degradation of carbohydrates and other labile components. However, the study also showed that soil fungi numbers and activity also increased in the warmer soil, with a corresponding rise in abundance of lignin-derived compounds (reflecting decomposition by the fungi). “The implication of the increased degradation of lignins is that less carbon remains in the soil solid phase, and more CO₂ is being released from the soil into the atmosphere,” Simpson says.

Conversely, certain other recalcitrant molecular structures—such as the alkyl structures found in the waxy coating or cuticles of leaves—remained resistant to decomposition and accumulated in the warmer soil. Thus, says Simpson, as global temperatures warm and more organic matter from litterfall is added to the soil, less of that matter will be in a form that's easily used by microbial decomposers in the soil, including many soil bacteria that are needed to sustain robust plant life. “In other words, the soil's molecular carbon composition is shifting [toward] a form that is not usable to microbes or plants, and more of the remaining carbon is being derived from leaf cuticles that persist in the soil,” she says.

“[The Simpson study] raises some interesting points,” says Jerry Hatfield, who directs the U.S. Department of Agriculture National Soil Tilth Laboratory. “Research already indicates that as you move from northern climes to southern and temperatures increase, it becomes more difficult to increase the organic material in soil.”

Howard Epstein, an associate environmental science professor at the University of Virginia, urges caution in interpreting the study's findings. “The experiments in this paper provide very short-term results,” he says, “and often



initial responses are not sustainable in the future. Systems adjust, and it is unreasonable to imply that litterfall from plants will increase with warming as suggested and remain high, [and] it is also unreasonable to assume that decomposer communities will not adapt to changing dead organic substrates.”

Indeed, says Simpson, increased litterfall itself may be a short-term observation, “because as nutrients in the soil decline, so will plant growth.” The take-home message, she says, is that global warming may change the composition of soil organic matter, leading to shifts in the ability of soil to sustain plant and microbial life.

The authors note that their observations in the moist, sandy loam soil of the Canadian forest may not apply to soil biogeochemical processes in dry areas or soils with high clay contents. Moreover, they did not measure nutrient levels or CO₂ releases directly, and Simpson notes there is no set soil temperature increase that is expected to occur uniformly around the world. Nevertheless, she says, “we found an increased degradation of some soil organic matter components whose endpoint is CO₂, so CO₂ levels would increase with higher rates of degradation.”

Until now, soil-climate research has focused heavily on the total amount of carbon in the soil, but Simpson believes the more relevant issue may be changes in the carbon-based molecular structures contained in the soil's organic matter and how such changes will ultimately affect both microbial and plant life. “To understand the soil-climate interactions better, we will need more soil research to focus on the molecular level with an eye toward predicting both short- and long-range changes in the system,” she says. —Lance Frazer

INNOVATIVE TECHNOLOGIES

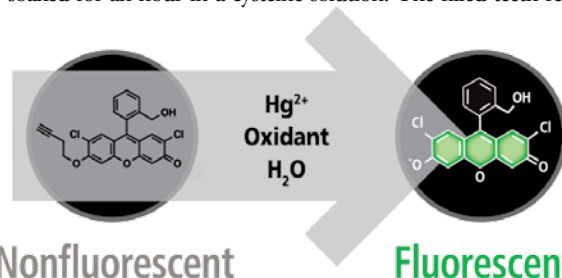
Fluorescent Probe Detects Mercury

Mercury is toxic to the nervous system and may cause memory loss, cognitive and behavioral disturbances, headaches, insomnia, peripheral nerve damage, tremors, and motor dysfunction—all problems that have been observed to disappear upon removing the source of mercury exposure, according to the International Programme on Chemical Safety. Removing the source may now become easier with a new chemical probe that gives off a bright green glow when it reacts with mercury in fish and dental amalgams. Eventually the probe could be used to detect contaminated fish at home or mercury in wastewater at dental offices.

Developer Kazunori Koide, an associate professor in the University of Pittsburgh Department of Chemistry, based the probe on a simple principle taught in undergraduate organic chemistry classes: Mercury converts alkynes into ketones. Koide's team synthesized an alkyne-based compound from commercial dichlorofluorescein. When mercury converts the alkyne into a ketone, the reaction generates a green fluorescent signal whose intensity corresponds to the amount of mercury present. "It's a very straightforward approach," Koide says, "yet no one ever thought to do this."

The probe performed well in real-life tests described in the 10 December 2008 issue of the *Journal of the American Chemical Society*. A piece of salmon about the size of a dime was first treated with an oxidizing agent to release mercury bound up as methylmercury, then was soaked in the alkyne test solution. Within 30 minutes, mercury in the sample had converted the test solution to a ketone, which produced a strong fluorescent signal. Next, the researchers soaked a thin cloth with saliva and pressed it against an extracted tooth filled with silver amalgam (which may contain up to 50% mercury) obtained from a dental clinic. When the solution was applied to the cloth, its green fluorescent signal was substantially brighter than that of a control cloth also treated with saliva but not held against the tooth.

Because the sulfur-containing amino acid cysteine is known to bind tightly to mercury in fish, Koide wondered whether cysteine in sulfur-rich foods such as onions and eggs would react with mercury in dental amalgams. In another experiment, two extracted teeth containing amalgams were soaked for an hour in a cysteine solution. The filled teeth released



a significant amount of mercury into the cysteine solution as compared with teeth that had been soaked in water at a temperature of 35°C.

Other probes for mercury reported in the scientific literature are largely based on chemical reactions between mercury and sulfur groups. However, sulfur-based tests are prone to oxidation during storage, making them impractical for environmental testing. The standard method for detecting mercury in environmental samples—atomic absorption spectrometry—is expensive. "We're not trying to compete with atomic absorption spectrometry," says Koide. "We want to fill a gap by making a probe that the general public can use."

Koide's fluorescent probe "provides a clever chemical approach for detecting mercury in complex samples," says Chris Chang, an assistant professor of chemistry at the University of California, Berkeley. "The simplicity and sensitivity of this assay are promising for further application." Koide and colleagues hope to turn this chemical tool into a kit, and are modifying the method to make it consumer-friendly, such as finding safe chemicals to transform extremely toxic methylmercury in fish into less toxic mercury species before testing. —Carol Potera

Kazunori Koide, Joseph Tart/EHP

The Beat

by Erin E. Dooley

Post-Tsunami Coral Comeback

In December 2004, coral populations were devastated by the deadly tsunami that swept across the Indian Ocean. A new survey by the World Conservation Society found high densities of baby corals in 60 tsunami-

ravaged locations in Aceh, Indonesia. The coral comeback is being linked to natural colonization by more resilient coral species along with a decline in drastic fishing practices such as the use of dynamite. In addition, transplanting baby corals from healthy wild coral has proved to be a more effective strategy than direct seeding for restocking coral-depleted areas.

USDA Announces New Ecosystem Office

On 29 December 2008, Agriculture Secretary Ed Schafer announced the U.S. Department of Agriculture will, as directed by the 2008 Farm Bill, form a new Office of Ecosystem Services and Markets and create a federal Conservation and Land Management Environmental Services Board. These entities will assist the department in guiding the implementation of market-based approaches to conservation, such as compensating farmers, ranchers, and forest landowners for providing wildlife habitat, carbon storage, and scenic landscapes. The first service to be

examined by the new office will be carbon sequestration.

Australia Says No Endosulfan Ban

Despite concerns by domestic and international groups about the endocrine-disrupting effects and persistence in the environment of endosulfan, Australia will continue to allow the restricted use of this insecticide. This announcement was made in January 2009 by the Australian Pesticides and Veterinary Medicines Authority. In December 2008 Australia's closest neighbor, New Zealand, joined 54 other countries in banning endosulfan. The Stockholm Convention on Persistent Organic Pollutants will determine in October 2009 whether to do a final assessment on endosulfan, which could result in a global ban by 2011.

CPSC Revises Safety Act

In 2008, the Consumer Product Safety Improvement Act was enacted to bolster efforts to protect children from lead and phthalates in products such as toys and

Divers transplant corals off Aceh, Indonesia.



AP Photo/Binsar Bakkar, Brandi Sims

PHARMACEUTICALS

New Insights into Thalidomide

Thalidomide, a drug banned in some countries for nearly 50 years because it causes malformations in embryonic limb tissue, may be on the verge of a dramatic, if carefully circumscribed, reinstatement for use against a range of diseases. Its return to the fold may be aided by a new study in the 1 December 2008 issue of *Molecular Pharmaceutics* that further elucidates the mechanism by which thalidomide caused teratogenic effects. This understanding, in turn, may help prevent similar damage in new applications for the drug and its analogues.

First made in Germany in the 1950s, thalidomide was marketed as a sedative and anti-emetic. Rodent tests indicated thalidomide had low toxicity. It is now known, however, that most rats and mice are insensitive to the teratogenic effects of thalidomide, whereas humans, chickens, and rabbits are highly sensitive. By 1961 about 10,000 babies with severe limb malformations had been born to women who took the drug while pregnant, and thalidomide was removed from the market.

Interest in thalidomide continued, however. Today, cancer researchers are very interested in thalidomide's cancer-curbing potential, which has been primarily associated with the inhibition of angiogenesis, the growth of new blood vessels recruited by the tumor. The U.S. Food and Drug Administration approved the drug in 1998 for treating the skin lesions associated with leprosy and in 2007 for treating newly diagnosed multiple myeloma, as long as strict protocols to prevent pregnancy are followed in female patients of child-bearing age. A number of small-scale studies have suggested the drug would be effective against other inflammatory diseases including rheumatoid arthritis, inflammatory bowel disease, and mucous membrane ulcers in HIV-positive patients.

The *Molecular Pharmaceutics* report, by Jürgen Knobloch and colleagues at Heinrich-Heine-University in Düsseldorf, Germany,

builds on earlier work by the team showing that thalidomide triggers massive apoptosis in embryonic tissue responsible for outgrowth of the limbs. This cell death results from production of reactive oxygen species (ROS), leading to overwhelming oxidative stress in those cells.

In the current study, Knobloch and colleagues dosed chicken, human, and mouse embryonic fibroblasts with thalidomide and, after an incubation period, measured the cells' levels of superoxide, a powerful free radical. They also measured levels of glutathione, a major antioxidant inside cells that affords protection against superoxide and other ROS.

As expected, the human and chicken fibroblasts were unable to neutralize the ROS and ward off cell death. Because thalidomide caused so many cells to die, the embryonic limb buds failed to develop properly. The mouse fibroblasts were able to produce enough antioxidants to protect the developing tissue, but the researchers also found that if they depleted glutathione in these cells, the effects were similar to those in the thalidomide-sensitive species.

Many scientists now speculate that thalidomide's therapeutic promise against various diseases ultimately will be fulfilled not by the drug itself, but by analogues that do not share its undesirable effects. "It is clear that prolonged exposure results in unacceptable neurotoxicity," says W. Douglas Figg, head of the Molecular Pharmacology Section and the Clinical Pharmacology Program of the National Cancer Institute's Medical Oncology Branch. "There are still unanswered questions, especially [regarding] the relationship between birth defects and anticancer effects."

Knobloch considers answering those questions "a prerequisite for developing efficient thalidomide derivatives for cancer and inflammation-based diseases." His team is now investigating thalidomide's anti-inflammatory effect in hopes of clarifying the associated mechanism and eventually finding treatments for inflammatory lung diseases. —Valerie J. Brown



Secondhand toy sales will be governed by good sense, not legislation.

clothing. In response to concerns expressed by thrift store owners and purveyors of handmade toys, the Consumer Product Safety Commission voted in January 2009 to refine the act—for example, by relieving thrift shops of the need to test used goods for lead and phthalates. However, resellers and parents alike should avoid selling or buying used products that are likely to contain lead or phthalates.

New Tests Lower Lab Animal Needs

The U.S. Interagency Coordinating Committee on the Validation of Alternative Methods (ICCVAM) has endorsed two standardized, oral, cell-based tests to help companies determine the potential hazards of chemicals. The new methods measure cell death and can determine the first dose to test in animals. Acute oral toxicity tests are currently the most commonly used toxicity tests used in animals worldwide, and the new tests could greatly reduce the numbers of lab animals needed for such tests. ICCVAM is seeking incorporation of the test recommendations in guidance to be issued by the Organisation for Economic Co-operation and Development (OECD), which will go to OECD's 30 member countries.

Lights Out for Low-Efficiency Bulbs

In a move that could dramatically curb carbon emissions and European household energy costs, the European Union (EU) is now moving forward with formal legislation to ban low-efficiency light bulbs by 2012. The first phase of the legislation will begin in September

2009, when bulbs with a light output of 100 watts or more must achieve at least a C-class efficiency rating—a requirement that incandescent bulbs of this wattage will be unable to meet. The regulations will continue to be implemented in stages until all classes of bulbs have at least a C-class rating. According to an EU technical briefing on the new legislation, lighting can represent up to one-fifth of a household's electricity consumption.



Amsterdam, Netherlands. European lighting will go high-efficiency by 2012.